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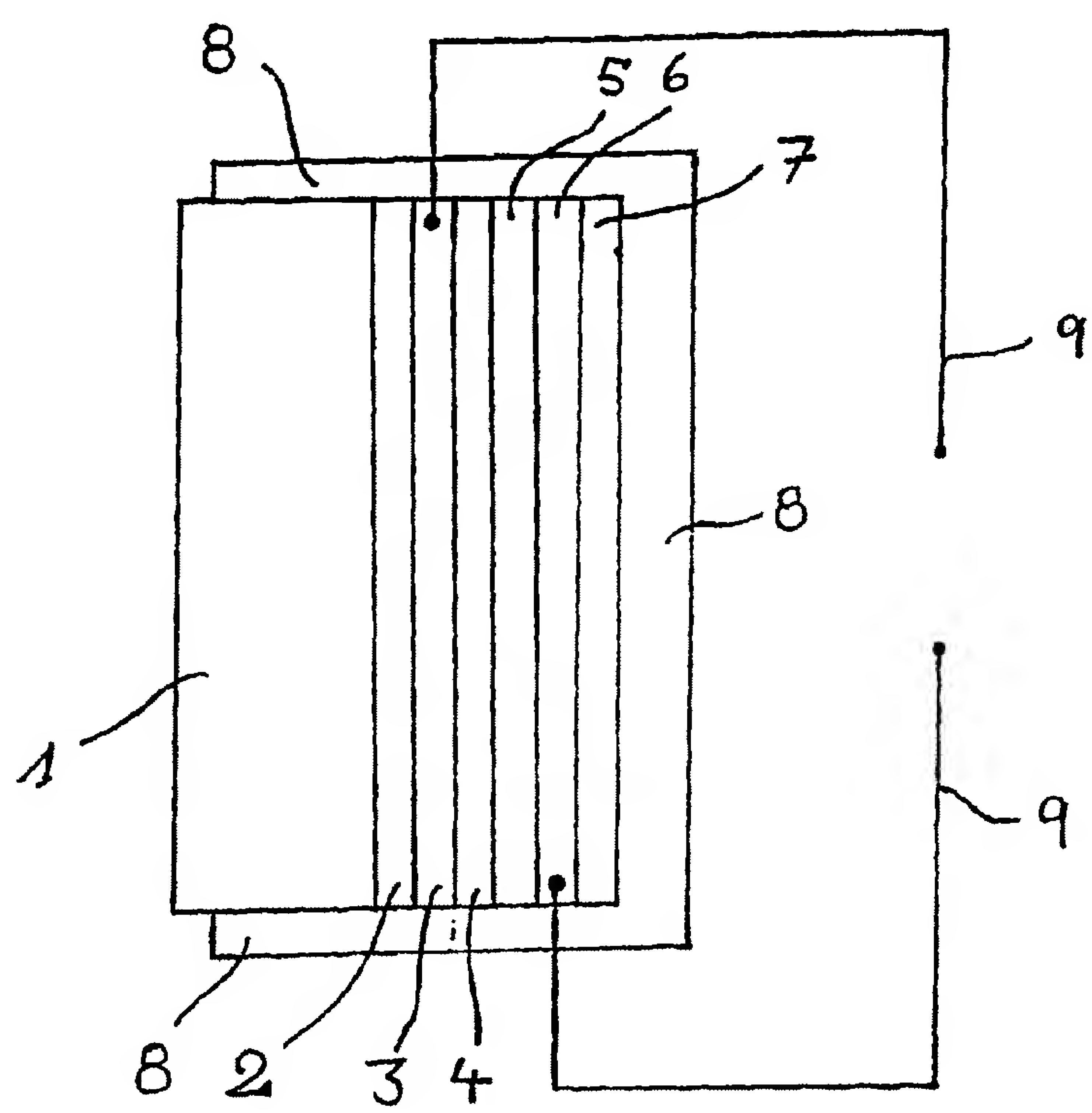
(54) Title: ELECTROCHROMIC GLASS COMPONENT

(57) Abstract

The invention relates to an electrochromic glass component, particularly for motor vehicle mirrors, which contains a doped ion–conducting basic polymer (4) as the ion–conducting layer. The electrochromic glass component consists, for example of a glass substrate (1) as well as a layer system having an electrochromic layer (2), a mirror layer (3), a doped polymer membrane (4), for example of polybenzimidazole polymer, a proton store (5), a rear electrode (6) and a polyester film (7). The layer system is sealed by a seal (8) which closes the coating system towards the glass substrate (1).



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Electrochromic glass component

FIELD OF INVENTION

The invention relates to an electrochromic glass component, particularly for motor vehicle mirrors, which contains a doped ion-conducting basic polymer as the ion-conducting layer.

BACKGROUND OF INVENTION

Electrochromic mirrors, particularly for motor vehicles, are known in the state of the art. The essential element of these electrochromic mirrors is a layer of electrochromic material. A material is termed electrochromic when it changes its optical constants (n, k) and hence its optical properties on application of an electric field. Typical examples of such electrochromic materials are WO_3 and MoO_3, which are virtually colourless when applied to a substrate in thin layers. An electrochromic layer may change its optical properties by oxidation or reduction processes. If protons move in such a layer, in the case of tungsten oxide there is a reduction to blue tungsten bronze. The intensity of colouration is determined by the quantity of charge which has flowed in the layer.

Numerous electrochromic mirrors, particularly for motor vehicles, are now know from the state of the art and have electrochromic layers of this type in different layered structures.

German 3 008 768 describes an electrochromic mirror which essentially consists of a layer system built on

a glass substrate at least one electrochromic layer, at least two electrodes, at least one proton-conducting layer and at least one proton-delivering and one proton-storing layer being present.

The optical change properties of a mirror of this type are determined, inter alia, by the proton conductivity of the proton-conducting layer. The higher the proton conductivity, the higher also the rate of change of reflection. In the mirrors of the state of the art, proton-conducting glass plates, which were soaked with sulphuric acid, have been used hitherto as proton-conducting layers (for example in German Offenlegungsschrift 2 504 905) or as in German 3 008 768 so-called solid ion-conducting layers.

It has been shown all these ion-conducting layers from the state of the art used hitherto for the electrochromic glass components still do not have satisfactory results with regard to ion conductivity. Furthermore, it is disadvantageous for the mirrors of the state of the art, that the ion-conducting layers described there are either too thick or are too complex and expensive as regards their mode of manufacture.

SUMMARY OF INVENTION

The object of the present invention is therefore, starting from the electrochromic mirror as described in german 3 008 768, to indicate a significantly improved embodiment which is characterised particularly by an ion-conducting layer which is favourable to apply as regard to manufacture and processing and furthermore has a high ion conductivity, with which

it is possible to change the electrochromic layer quickly.

The invention is achieved by the characterising features of patent claim 1. The sub-claims show advantageous further developments.

According to the invention it is thus proposed to use a doped ion-conducting basic polymer as the ion-conducting layer. It has been shown that these doped ion-conduction basic polymers are particularly well suited. The doped ion-conducting basic polymer is preferably selected from polybenzimidazoles (PBI), polypyridines, polyimidazoles, polybenzthiazoles, polybenzoxazoles, polyquinolines, polythiazoles, polyoxadiazoles and polytetrapyrenes. The ion-conducting layer is thus a layer which preferably conducts protons. However, in principle the layer is also suitable for other ions, such as for example lithium.

DESCRIPTION OF THE DRAWINGS

The invention is illustrated in more detail below using Figure 1 and Figure 2.

Figure 1 shows an electrochromic glass component of the invention, here as a motor vehicle mirror.

Figure 2 shows the concrete structure of a mirror.

DESCRIPTION OF THE INVENTION

The electrochromic glass component, which is used as a motor vehicle mirror, consists of a glass substrate

1 having a thickness of 2 mm. A layer system which has the following successive layers is applied to this substrate 1.

An electrochromic layer 2 of tungsten oxide having a thickness of ~ 700 nm, a mirror layer 3 of palladium having a thickness of ~ 70 nm, a polymer membrane 4 of polybenzimidazols polymer having a thickness of 30 μm, a proton store 5 of tungsten trioxide having a thickness of 700 nm, a rear electrode 6 of gold having a thickness of 100 nm, a polyester film 7 having a thickness of about 175 μm as well as a sealing layer 8 of traditional plastics, which wraps around the entire coating system including the glass substrate 1 and thus seals the coating system comprising layers 2 to 7. Seal 8 is only interrupted by copper wires 5, which contact the mirror layer 3 on the one side and the rear electrode 6 on the other side to apply a voltage to the latter.

Figures 2a and 2b show the electrochromic glass component according to Figure 1, but the function of a glass component of this type becomes visible here. In the exemplary embodiment according to Figure 2, a primer 10 for better adhesion promotion is also applied between the electrochromic layer 2 and the mirror layer 3. Figure 2a thus shows the light position and Figure 2b the dark position.

It is particularly preferable for the electrochromic glass component of the invention if the doped ion-conducting polymer is present in the form of a polymer membrane. A proton-conduction polymer membrane particulate preferred. It should be emphasised in particular for the ion-conducting layer according to

the invention that it may be applied easily using all conventional techniques. Examples of these are screen printing, immersion, spraying, blade coating or also application of a gel.

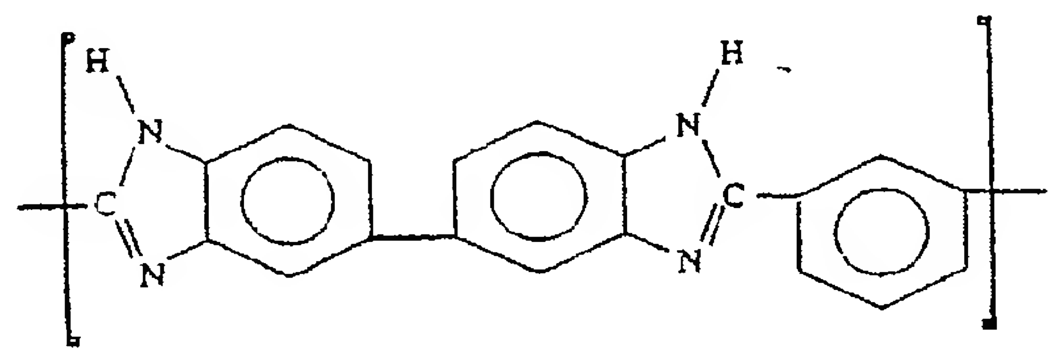
According to the present invention it is particularly preferable if the polymer membrane is a polybenzimidazole.

It should be emphasised in particular for the electrochromic glass component of the invention that the doped ion-conducting layer has particularly good properties with regard to its ion conductivity if the ion-conducting layer is doped with an acid, in particular with a strong acid. It is preferable if the pKa value of the doping acid ≤ 4.5, preferably ≤ 3.5 for the first dissociation stage at 25 °C. For acid it has proved to be particularly advantageous if the acid is a phosphoric acid, in particular a polyphosphoric acid. Acid treatment of polybenzimidazoles is described in United States 5 599 639, to which reference is made expressly here.

It is particularly preferable for the electrochromic glass component of the invention if it contains a proton-conducting polymer membrane of polybenzimidazole.

Polymer membranes of this type, which are composed of polybenzimidazoles and are proton-conducting, are known from the state of the art, for example from United States 5 017 681. All named polybenzimidazoles in the above-mentioned United States patent specification may be used in principle for the proton-conducting layer of the invention. It is particularly

preferable if the polymer consists of a polybenzimidazole having a molecular weight between 1,000 and 500,000 which consists of repeating units of the following structural formula:



It has proved to be particularly favourable for the electrochromic glass component if the ion-conducting layer described in more detail above is used at a layer thickness of 1 μm to 1 mm, preferably 5 μm to 100 μm. Application of the layer, in particular the polymer membrane, may thus be effected by screen printing, immersion, spraying, blade coating or even as a gel. Provision is thus made according to the invention in that the layer is applied either as a finished film or is even produced directly on the substrate or a layer lying underneath. These application procedures may also be used in combination.

The electrochromic layer, which preferably has a layer thickness of 300 nm to 8,000 nm, preferably 300 nm to 8,000 nm, preferably consists of WO_3, MoO_3, IrO_2 or mixed oxides thereof. The electrochromic layer is applied by sputtering, sol-gel or by vapour deposition.

The electrodes, which are necessary for constructing the layer system of the invention, are preferably

metallic layers having a layer thickness of 50 nm to 10 μm. Examples of layers of this type are those which contain rhodium, palladium. platinum or alloys thereof.

According to a preferred embodiment, provision is made in that a metallic electrode layer at the same time forms a reflector which may accept protons. This reflector preferably consists of a layer having a layer thickness of 30 nm to 500 nm, which contains rhodium, palladium, platinum or alloys thereof.

As already described in German 3 008 768, it is also preferable for the electrochromic glass component of the invention if the ion-delivering layer and the ion-storing layer at the same time form a layer or a composite. According to a preferred embodiment of the invention, provision is thus made in that the proton-storing layer is the electrochromic layer at the same time. In this case, for example a WO_3 layer, thus functions at the same time as a hydrogen ion-storing layer and as an electrochromic layer. According to a preferred embodiment, the composite consists of the proton-storing and at the same time proton-delivering layer on a film, preferably a polyester film with metallisation which is the counter-electrode. Instead of the film of polyester, glass, metal or other plastics are suitable as substrate materials for the composite.

With regard to the possible layered structure variants of the electrochromic glass component of the invention, reference is made to German 3 008 768 and the layered structure described therein.

However, it is preferable for the glass component of the invention if the glass component has been constructed from two layered composites. Hence, in the manufacture of the electrochromic glass component according to a preferred embodiment, a first layer system is constructed on a glass substrate, an electrochromic layer applied thereto and metallisation as a reflector. These layers are produced by means of sputtering processes.

The second part of the layer system is then a composite which consists of a proton-storing layer, metallisation and a film arranged thereabove, in particular a polyester film. This composite is manufactured in a separate process step and then joined to the above-mentioned first layered composite of the layer system. This procedure facilitates cost-effective and simple manufacture of the electrochromic glass component.

A further favourable embodiment of the invention makes provision, if it is necessary, in that adhesion-promoting layers for better bonding are applied between the individual layers. Examples of this are chromium, titanium or even silicon oxides SiO_x. For application as motor vehicle mirrors, provision is also made in that the layer system is tightly sealed externally. Hence the layer system may be sealed at the and-faces and a final layer, that is a layer opposite the glass substrate seen in the viewing direction, may be provided with a protective layer, for example a diffusion barrier. Diffusion barriers of this type have a water permeability < 1,000, preferably < 100 cm^3. For motor vehicle mirrors it has proved to be particularly favourable if

the glass substrate is a reflection-reducing thin glass having a layer thickness of 0,1 to 3 mm. For motor vehicle mirrors it is also advisable if a transparent conductive layer for heating the mirror is applied in front of the substrate, seen in the viewing direction.

Patent claims

1. Electrochromic glass component, particularly for motor vehicle mirrors, having a layer system arranged on a glass substrate containing at least one electrochromic layer, at least two electrodes, at least one ion-conducting layer, at least one ion-delivering layer and at least one ion-storing layer, wherein the two last-mentioned layers may also form a layer at the same time, characterised in that the ion-conduction layer contains a doped ion-conducting basic polymer.

2. Electrochromic glass component according to claim 1,
characterised in that the doped ion-conducting polymer is selected from polybenzimidazoles, (PBI), polypyridines, polyimidazoles, polybenzthiazoles, polybenzoxazoles, polyquinolines, polythiazoles, polyoxadiazoles and polytetrapyrenes.

3. Electrochromic glass components according to claim 1 or 2,
characterised in that the doped ion-conducting polymer is a polymer membrane.

4. Electrochromic glass component according to claim 3,
characterised in that the polymer membrane consists of a polybenzimidazole polymer.

5. Electrochromic glass component according to at least one of claims 1 to 4, characterised in that the ion-conducting layer is doped with acid.

6. Electrochromic glass component according to claim 5, characterised in that the layer has been doped with phosphoric acid.

7. Electrochromic glass component according to at least one of claims 1 to 5, characterised in that the pKa value of the free acid is ≤ 4.5 at 25 °C for the first dissociation stage.

8. Electrochromic glass component according to at least one of claims 1 to 7, characterised in that the ion-conducting layer has a layer thickness of 1 μm to 1 mm.

9. Electrochromic glass component according to at least one of claims 1 to 8, characterised in that the ion-conducting layer is applied to the substrate or a different layer of the layer system or is produced thereon.

10. Electrochromic glass component according to at least one of claims 1 to 9, characterised in that the ion-conducting layer is applied or produced by screen printing, immersion, blade coating, spraying or as a gel, or by a combination thereof.

11. Electrochromic glass component according to at leastone of claims 1 to 10, characterised in that the electrochromic layer is an oxidation-reduction layer consisting of metal oxides.

12. Electrochromic glass component according to claim 11, characterised in that the electrochromic layer is a WO_3 layer having a layer thickness of 100 nm to 3,000 nm.

13. Electrochromic glass component according to at least one of claims 1 to 12, characterised in that at least one electrode is designed in the form of metallic layers having a layer thickness of 100 nm to 10 μm.

14. Electrochromic glass component according to claim 13, characterised in that a metallic electrode layer forms a reflector which may accept and conduct protons at the same time.

15. Electrochromic glass component according to at least one of claims 1 to 14, characterised in that the ion-delivering and ion-storing layer is present in the form of a composite.

16. Electrochromic glass component according to claim 15, characterised in that the composite consists of a substrate, for example of glass, metal or plastic, for example a polyester film, to which

a proton-storing layer, for example a metal oxide layer, is applied.

17. Electrochromic glass component according to claim 16, characterised in that the composite additionally has an electrode layer in the form of metallisation.

18. Electrochromic glass component according to at least one of claims 1 to 17, characterised in that an electrochromic layer, metallisation as a reflector, a proton-conducting membrane and a composite of a proton-storing layer, metallisation and a film arranged thereon, in particular of polyester, is applied to a glass substrate one after another, seen in the viewing direction.

19. Electrochromic glass component according to claim 18, characterised in that the layer system is sealed at the end-faces,

20. Electrochromic glass component according to claim 18 or 19, characterised in that the final layer opposite the glass substrate is provided with a protective layer.

21. Electrochromic glass component according to one of claims 19 or 20, characterised in that a reflection-reducing thin glass having a layer thickness of 0.3 to 3 mm is used as the glass substrate.

22. Electrochromic glass component according to one of claims 19 to 21, characterised in that a conductive layer for heating the mirror is applied in front of the substrate, seen in the viewing direction.

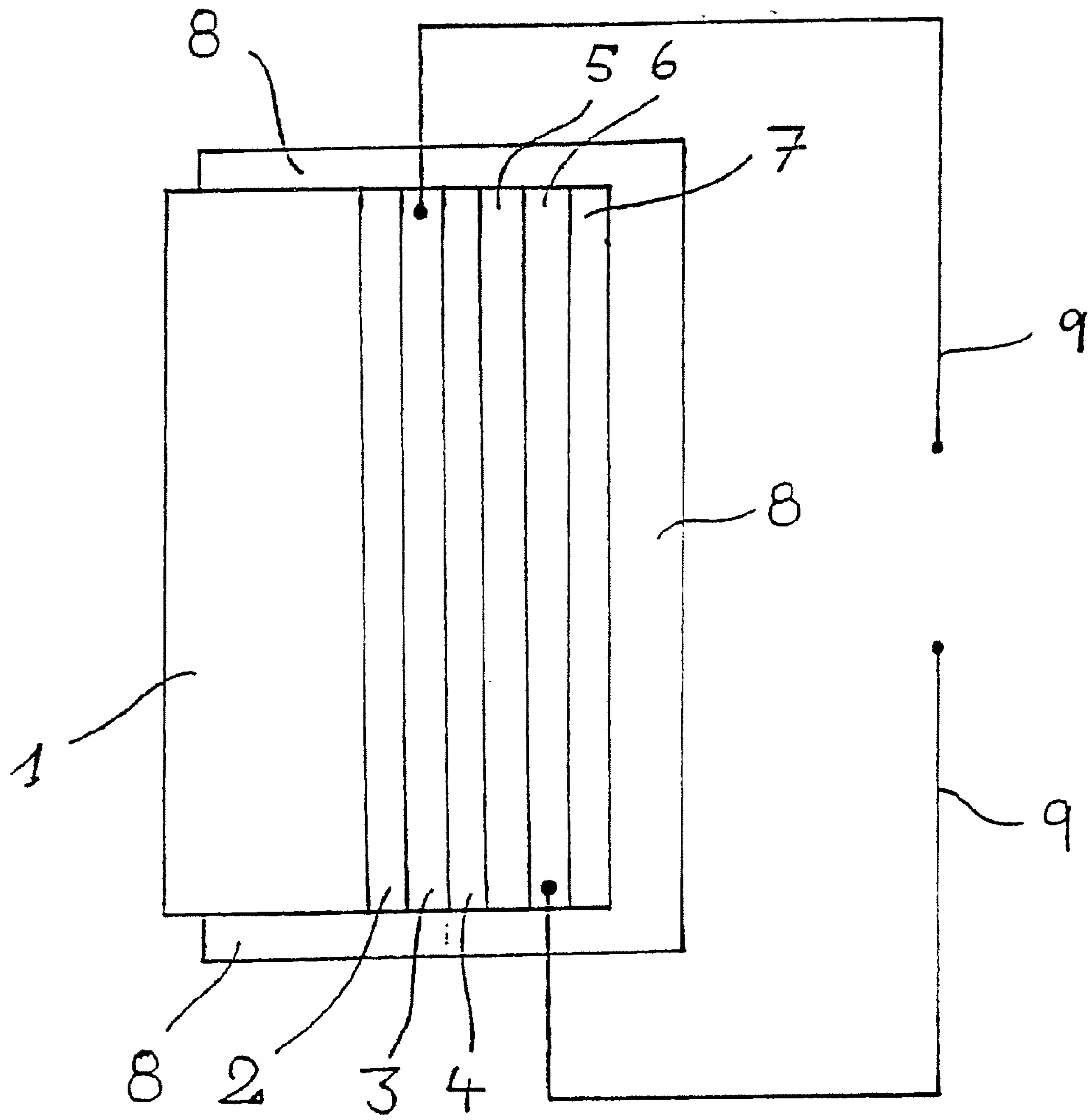


Fig. 1

FIG. 2a

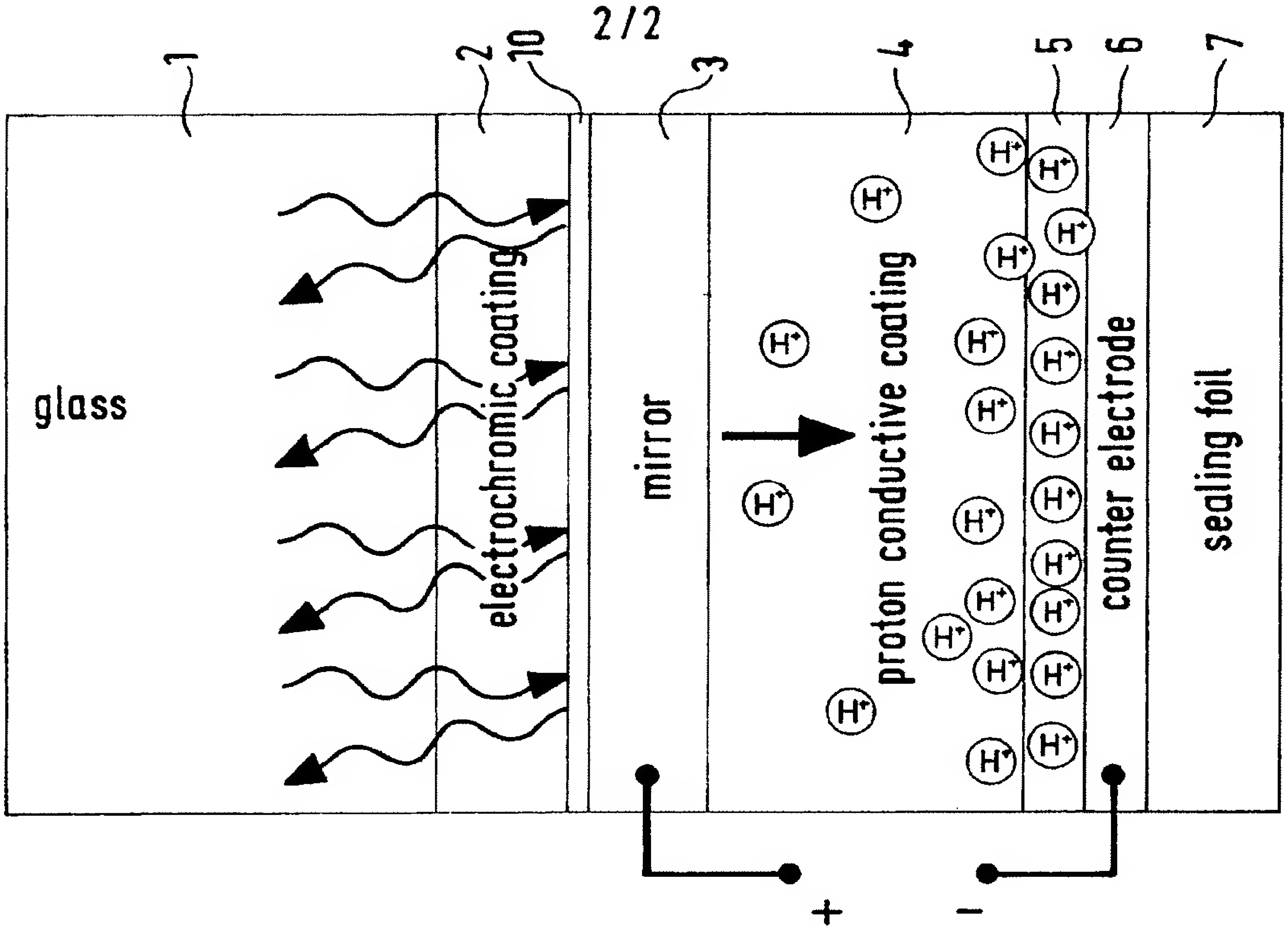

glass
electrochromic coating
mirror
proton conductive coating
counter electrode
sealing foil
1
2
10
3
4
5
6
7
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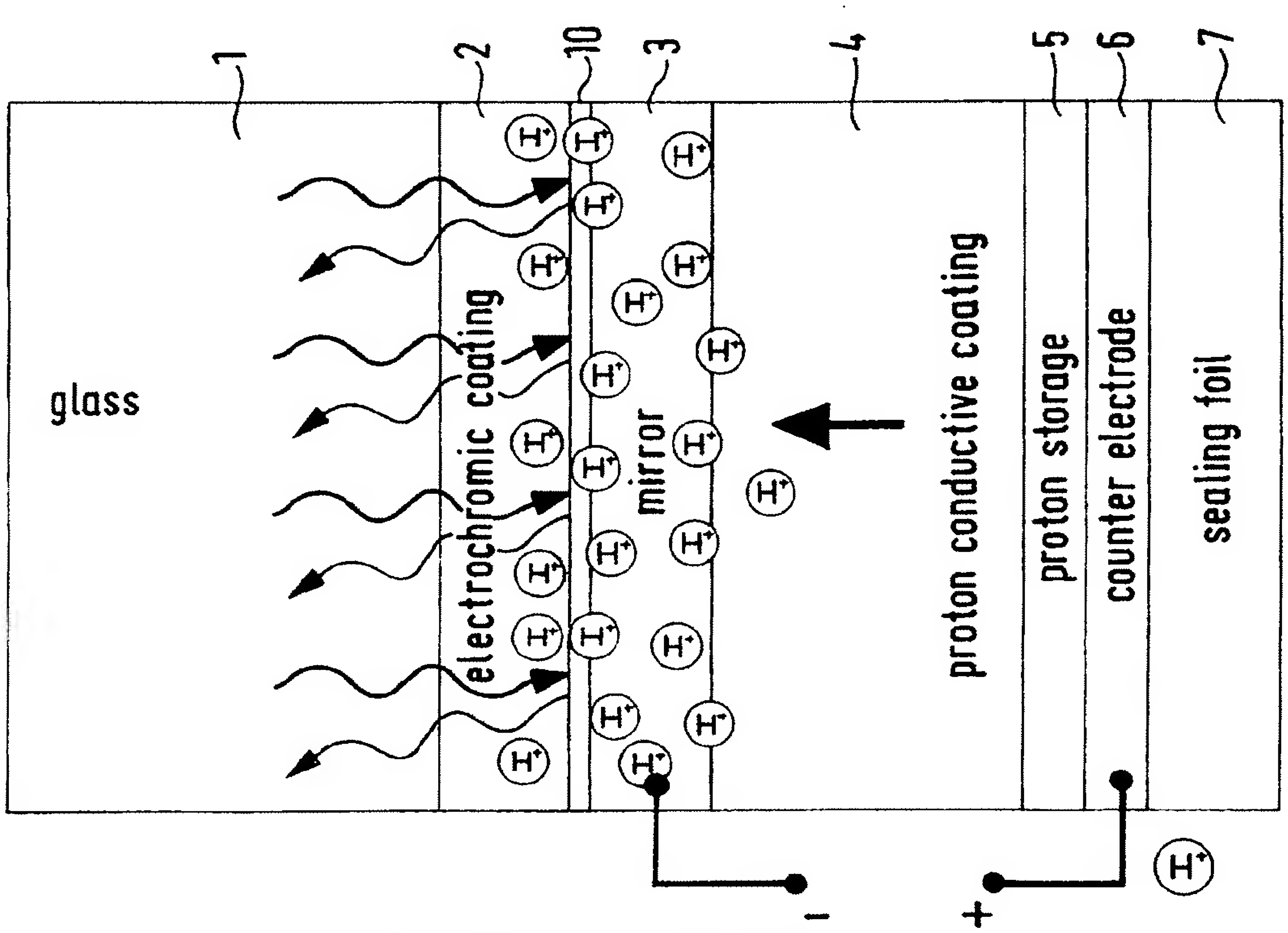
FIG. 2b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mirror
proton conductive coating
proton storage
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/08572

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G02F1/15

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	EP 0 483 893 A (GEN MOTORS CORP) 6 May 1992 (1992-05-06) column 1, line 1 - line 10 column 2, line 53 - line 57 column 6, line 6 - line 38 ---	1,3,5, 7-22
A	EP 0 450 581 A (SONY CORP) 9 October 1991 (1991-10-09) column 3, line 14 - line 20 column 4, line 23 - line 29 column 12, line 12 - line 20 --- -/--	2

[X] Further documents are listed in the continuation of box C.

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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A	US 5 536 808 A (CURTIS M DAVID ET AL) 16 July 1996 (1996-07-16) column 1, line 15 - line 19 column 1, line 65 -column 2, line 3 column 3, line 21 - line 25 -----	2

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/EP 99/08572

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